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METHANESULFONATE AND NON-SEA-SALT SULFATE IN DRIFTING-SNOW FROM EAST QUEEN MAUD LAND, EAST ANTARCTICA

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Abstract: Drifting-snow samples were collected at Mizuho Station from February to September 1986 and along traverse routes in east Queen Maud Land, East Antarctica, from October 1986 to January 1987. The typical sampling interval was about once a week. Variability in the methanesulfonate (MSA) and non-sea-salt (nss) SO_4^{2-} concentration levels suggests a seasonal relationship: high in summer and low in winter. The ratios of $nssSO_4^{2-}$/MSA concentrations show a weak inverse seasonal relationship. The concentration levels of $nssSO_4^{2-}$ correlate well with MSA concentration levels in the Mizuho Station samples obtained from late summer to early spring, suggesting that the dominant source of the $nssSO_4^{2-}$ and MSA deposited in this region is marine biogenic dimethylsulfide.

On the other hand the $nssSO_4^{2-}$/MSA ratios from the traverse samples are significantly higher and deviate widely from the Mizuho Station regression line, implying a non-biogenic natural source for the $nssSO_4^{2-}$ at the higher elevation inland locations.

1. Introduction

Sulfate is a major ionic constituent in aerosols and precipitation. Major natural sources of sulfate in aerosols in remote marine area include sea salts, oxidation of reduced sulfur compounds such as dimethylsulfide (DMS) and oxidation of SO_2 from volcanic origin (WARNECK, 1988). In the remote southern troposphere including coastal areas of Antarctica, marine biogenic DMS is generally accepted as the dominant source of submicron non-sea-salt SO_4^{2-} ($nssSO_4^{2-}$) in aerosols and in snow (PROSPERO *et al.*, 1991; SAVOIE *et al.*, 1993). Major oxidation products of DMS under atmospheric conditions include methanesulfonate ($CH_3SO_3^-$) and SO_2 (HATAKEYAMA *et al.*, 1982). Unlike $nssSO_4^{2-}$, which has non-marine biogenic sources such as volcanic SO_2, methanesulfonate ($CH_3SO_3^-$, MSA) is a unique oxidation product of marine biogenic DMS. In remote atmospheres, concentration levels of MSA and ratios of $nssSO_4^{2-}$/MSA have been used to trace the relative contribution of $nssSO_4^{2-}$ from the marine biogenic DMS (SAVOIE *et al.*, 1989, 1994; PROSPERO *et al.*, 1995), although the oxidation processes from DMS to end products are not yet well understood. For example, the ratios for aerosol samples obtained from the marine boundary layer at high-latitudes are lower than those in mid- to low-latitudes (BATES *et al.*, 1992). Although results from laboratory experiments suggest a temperature dependence of the branching ratio in the DMS oxidation with higher MSA yield for lower temperature (HYNES *et al.*, 1986; HYNES and WINE, 1989), the natural latitudinal distribution of the ratios is not yet fully understood.

In Antarctica, MSA and $nssSO_4^{2-}$ concentrations have been measured on surface

snow and deeper ice core samples (IVEY *et al.*, 1986; SAIGNE and LEGRAND, 1987; LEGRAND *et al.*, 1992; KAMIYAMA *et al.*, 1992; MULVANEY *et al.*, 1992; WELCH *et al.*, 1993; UDISTI *et al.*, 1993; LANGWAY *et al.*, 1994; PASTEUR *et al.*, 1995). From these measurements, new information is available to more fully understand and interpret the polar MSA data. For example, it is reported (MULVANEY *et al.*, 1992; LANGWAY *et al.*, 1994) that distinct and regular seasonal variations (high concentration in summer and low concentration in winter) exist in the concentration levels of MSA and $nssSO_4^{2-}$ in snow samples from shallow snow depths but diminish in amplitude with increasing depth below the surface. Recent attention has also been given to the origin of non-biogenic $nssSO_4^{2-}$ deposits along coastal Antarctic areas (UDISTI *et al.*, 1993; SAVOIE *et al.*, 1993) as well as in pre-Industrial revolution periods in Greenland ice cores (HANSSON and SALTZMAN, 1993; OSADA and LANGWAY, 1993). Clearly more research on snow and ice samples from the Antarctic ice sheet is needed to understand more fully the sulfur cycle in the Antarctic region.

In previous papers we have discussed the results of in-situ liquid conductivity measurements (OSADA *et al.*, 1989), and major ionic concentration levels as they related to the oxygen stable isotope ratios found in snowdrift samples from Antarctica (OSADA, 1994). Short-term variations of major ionic constituents and general chemical properties of the snow samples were described in these papers. The present study focuses on seasonal and regional variations found in MSA and $nssSO_4^{2-}$ concentration levels of the snowdrift samples.

2. Sampling and Analysis

Snowdrift samples were obtained at Mizuho Station (70°42'S, 44°20'E, 2230 m) from February to September, 1986, and along oversnow traverse routes in east Queen Maud Land from 1800 to 3000 m above sea level from October 1986 to January 1987. Figure 1 is a location map of collection sites: Mizuho Station and the traverse routes. The study area is categorized as a cold katabatic region (DALRYMPLE, 1966), where severe drifting and blowing snow conditions frequently occur (KOBAYASHI, 1978; TAKAHASHI, 1985).

Under the cold and dry snow condition existing over most of inland Antarctic, snow deposits most commonly consist of a mixture of newly-fallen snow and wind drifted snow derived from mechanical wind erosion of the preexisting snow surface. This mixed and redeposited snow is called "snowdrift". In this study snowdrift was captured by placing a sampling bottle in a small pit.

Snow-trap sampling was carried out with special care wearing clean clothing, a clean face mask and powder-free clean PVC gloves to avoid contamination from snow vehicles, camp sites and human activities. Precleaned polypropylene and polyethylene wide-mouth sampling bottles were used to collect the samples. The sample bottles were sealed in double polyethylene bags and kept frozen during transport and storage until they were melted for chemistry analysis (see for details of sampling procedure in OSADA *et al.*, 1989; OSADA, 1994). After the initial chemistry measurements were completed the remaining sample aliquots were immediately refrozen and stored until they were measured for MSA.

All laboratory procedures included melting the field samples in a microwave

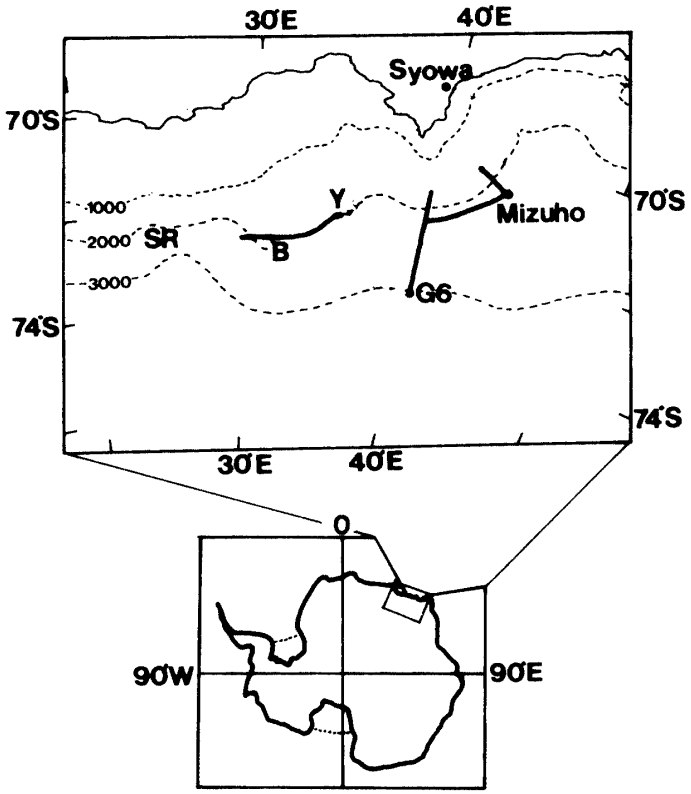

Fig. 1. Location map of sample collection sites. Trap sampling of drifting snow was conducted at Mizuho Station and along the traverse routes shown by thick lines. G6: glaciological observation sites, Y: Yamato Mountains, B: Belgicafjella and SR: Sør Rondane Mountains.

oven in the laboratory of STEL/Nagoya University immediately before chemical analysis. Concentration levels of MSA, SO_4^{2-} and Na^+ were measured by ion chromatography (Dionex, model DX-300) equipped with an AS11A analytical column and AG11 guard column for anion separation, and CS12 analytical column and CG12 guard column for cation separation. Using a 500 μl injection loop for each analytical flow system, procedural background concentration levels were below detection limits (0.5 ng/g for MSA, 3 ng/g for SO_4^{2-} and 0.5 ng/g for Na^+) in the present set-up.

3. Results and Discussion

3.1. Seasonal variations

Figure 2 shows the results of recent chemical analyses of the snowdrift samples collected at Mizuho Station (Fig. 2, column a) and along the traverse route (Fig. 2 column b). Non-sea-salt SO_4^{2-} ($nssSO_4^{2-}$) concentration is the non-sea-salt originated part of the total SO_4^{2-} content. The $nssSO_4^{2-}$ fraction is calculated from the measured SO_4^{2-} and Na^+ content in the samples as compared to the SO_4^{2-}/Na^+ ratio in sea water (0.25).

At Mizuho Station (Fig. 2a), the seasonal variations in the concentrations of MSA and $nssSO_4^{2-}$ of the snowdrift trapped samples show maxima in the austral summer with high variability and minimum in the winter with low variability. This is consistent with

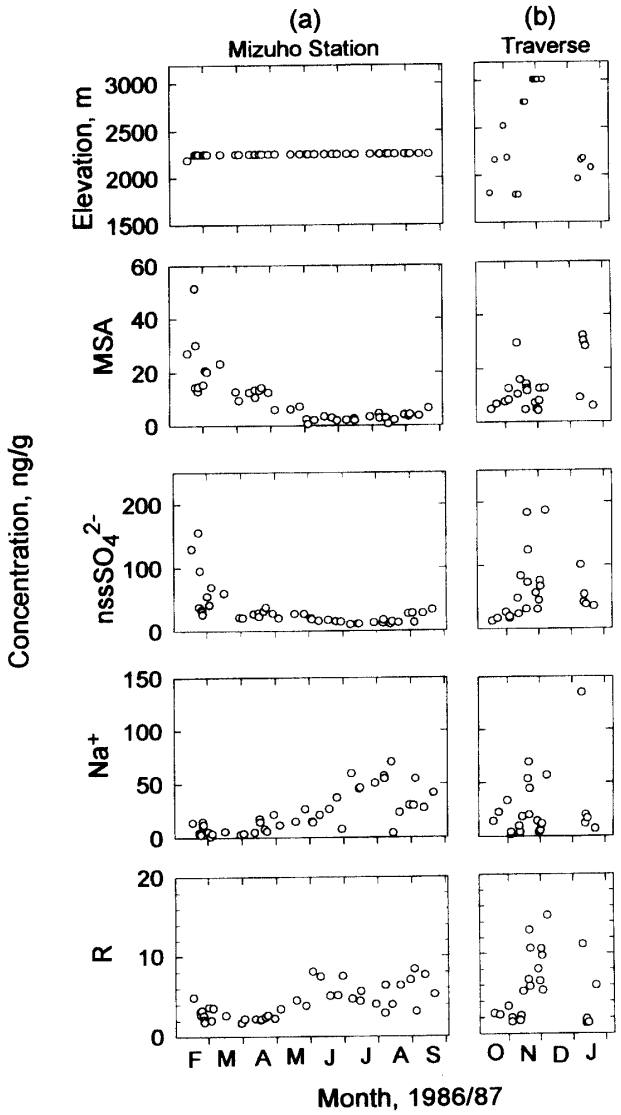

Fig. 2. Concentration levels (ng/g) of constituents and the ratio (R) of $nssSO_4^{2-}$/MSA as a function of time in months during 1986/87. Columns a and b represent results for Mizuho Station and traverse samples, respectively.

the results reported for snow deposited at shallow depths (MULVANEY *et al.*, 1992; UDISTI *et al.*, 1993; LANGWAY *et al.*, 1994) and of aerosols collected at coastal stations in Antarctica (SAVOIE *et al.*, 1993). This suggests that the snowdrift in this study is closely related to atmospheric aerosol chemistry and also reliably tracks seasonal variation trends in the atmosphere. At Mizuho Station the MSA curve shows a gradual decrease toward a winter minimum but the $nssSO_4^{2-}$ concentration levels decrease sharply in March. The amplitudes of the concentration levels for summer to winter averages are about one order of magnitude for MSA (about 10 to 50 ng/g for summer and about 1 to 6 ng/g for winter) and about 5 times for $nssSO_4^{2-}$ (about 30 to 150 ng/g for summer and about 20 to 30 ng/g for winter). The seasonal amplitude for MSA is about one order of magnitude close to that of atmospheric aerosols collected at Mawson, but about 1/2 to 1/3 of the amplitude

at Palmer Station (SAVOIE *et al.*, 1993). The seasonal variation in the Na^+ concentration at Mizuho Station shows higher values in winter but is consistently low from February to May. The ratio (R) of $nssSO_4^{2-}$/MSA shows only a weak seasonal variation: lower values in summer and higher values in winter at Mizuho Station.

No samples were obtained for the gaps shown between mid- to late-December along the traverse (Fig. 2b), since the traverse route crossed the bare ice fields in the Yamato Mountains area. In the vicinity of G6 (3005 m), concentration levels of MSA and $nssSO_4^{2-}$ are close to summer values at Mizuho Station but significantly higher values were obtained for the *R* obtained near the G6 location from late November to early December. The geographical pattern of higher *R* at high inland locations has also been reported by other studies (LEGRAND *et al.*, 1992; KAMIYAMA *et al.*, 1992). In addition to the high *R* values, occasional high concentration in Na^+ profile is also found even though G6 is located at the highest sampling elevation of the traverse.

Possible explanations for the variations given for *R* include: (1) the existence of different transport efficiency between $nssSO_4^{2-}$ and MSA due to preferential removal of the larger MSA aerosols before the smaller $nssSO_4^{2-}$ aerosols (BATES *et al.*, 1992), and (2) the possible additional contribution of $nssSO_4^{2-}$ from non-marine biogenic sources (SAVOIE *et al.*, 1993; UDISTI *et al.*, 1993).

3.2. *Origin of $nssSO_4^{2-}$ in high elevation snowfall*

The ratio, *R*, of $nssSO_4^{2-}$ / MSA has been used to estimate the relative contributions of marine biogenic DMS precursors and other precursors to the $nssSO_4^{2-}$ content of aerosols (SALTZMAN *et al.*, 1986; SAVOIE *et al.*, 1989, 1994; PROSPERO *et al.*, 1995). There is no significant anthropogenic $nssSO_4^{2-}$ sources of the aerosols and consequently the snow chemistry of Antarctica (CLAUSEN and LANGWAY, 1989; DELMAS, 1992), it is further assumed that the atmospheric oxidation pathway of DMS will result in a relatively constant ratio of the components and that deviations from this ratio may be attributed to contribution of natural $nssSO_4^{2-}$ from other sources (PROSPERO *et al.*, 1995).

Figure 3 shows a scatter plot of MSA versus $nssSO_4^{2-}$ concentrations in snowdrift. Filled circles represent samples obtained at Mizuho Station and open triangles indicate samples collected along the surface traverse. The regression line shown in Fig. 3 is calculated for samples from Mizuho Station only:

$$[nssSO_4^{2-}] = 4.4 + 2.8\ [MSA], \qquad (n=42,\ r=0.91) \qquad (1)$$

where $[x]$ denote concentration levels of the constituents in ng/g units, n is number of samples used and r is a correlation coefficient.

The concentrations of $nssSO_4^{2-}$ at Mizuho Station correlate well with the MSA concentrations, suggesting that $nssSO_4^{2-}$ in snowdrift at Mizuho Station is predominantly derived from marine biogenic DMS along with MSA. The slope (2.8) at Mizuho Station is close to the values for aerosols obtained at the coastal Antarctic sites (SAVOIE *et al.*, 1993). In contrast, data at points along the over snow traverse samples are scattered widely, especially for samples from locations at high inland elevation (G6). These points deviate significantly from the regression line for the normal DMS oxidation source for the Mizuho Station area.

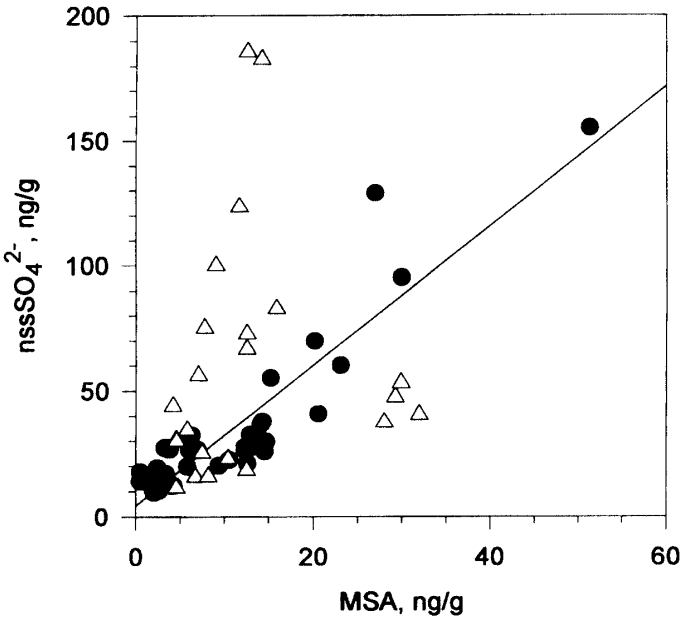

Fig. 3. Plot of $nssSO_4^{2-}$ versus MSA concentration levels in ng/g units. Filled circles represent data for Mizuho Station, and open triangles indicate data for traverse samples. Regression line is calculated for Mizuho Station only.

Potential sources for the natural non-biogenic contributions are required to have higher transport altitude to the high inland plateau area of Antarctica. Such sources and transport pathways may be different from the normal marine biogenic sulfur cycle at Mizuho Station area. Sporadic volcanic sources (LANGWAY *et al.*, 1994) and stratospheric background sulfuric acid (CUNNINGHAM and ZOLLER, 1981) are most likely to be additional sources for the high inland plateau area because both contributions may be transported well above the elevation of the marine boundary layer to high inland locations. Of various sources, a minor volcanic eruption of Ruiz volcano, Colombia, ejected SO_2 into the southern hemispheric stratosphere in November 1985 but the estimated amount of injected SO_2 is considered small (BLUTH *et al.*, 1993) and is not evident in optical depth records of the Antarctic atmosphere (HERBER *et al.*, 1993). At the same time, the contribution of stratospheric background sulfuric acid to the tropospheric sulfur budget seems to be small (CUNNINGHAM and ZOLLER, 1981). If no additional non-biogenic $nssSO_4^{2-}$ exists, as LEGRAND *et al.* (1992) assumed, transport from a low- to a mid-latitudinal biogenic source having higher R is needed to fit the observed high R in high inland plateau area.

It is still necessary to clarify whether non-biogenic $nssSO_4^{2-}$ exists in snow from the high inland plateau area. To do this, long-term collections for MSA and $nssSO_4^{2-}$ analyses of inland snow samples and aerosols are needed over the plateau area. This is necessary to understand the sulfur cycle in the high inland Antarctic plateau area and is important to properly interpret MSA data from ice cores.

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